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(71)Applicant : NITTO DENKO CORP

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(72)Inventor : MOROISHI YUTAKA
YAMAMOTO HIROKO
MURAKAMI YOSHIHIDE
INOUE TETSUO
YOSHIDA YOSHITOKU

(54) URETHANE-ACRYLIC POLYMER WATER DISPERSION AND ITS PRODUCTION

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a urethane-acrylic polymer water dispersion making a urethane-acrylic polymer stably dispersible into water without using an emulsifying agent, providing a filmed material of the dispersion having excellent water resistance, excellent strength and elongation characteristics, capable of readily designing these physical properties.

SOLUTION: A urethane-acrylic polymer hybrid water dispersion is prepared, then 80-10 wt.% of a monomer for nontackiness for a polymer consisting essentially of a (meth)acrylic acid alkyl ester and having ≥ 273 glass transition temperature based on 20-90 wt.% of the solid content of the dispersion is mixed thereto and the mixture is subjected to polymerization treatment to produce the objective urethane-acrylic water dispersion which is a room-temperature nontacky water dispersion of urethane-acrylic polymer composed of 10-50 wt.% of a polyol component, 2-20 wt.% of a polyisocyanate component and 40-90 wt.% of an acrylic monomer component, and provides a filmed material having ≥ 0.5 kg/mm² modulus of elongation and $\geq 300\%$ elongation at break in the tension test of the filmed material.

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CLAIMS

[Claim(s)]

[Claim 1] At a room temperature which consists of 10 to 50 % of the weight of polyol ingredients, 2 to 20 % of the weight of polyisocyanate components, and 40 to 90 % of the weight of acrylic components, by a water dispersing element of urethane acrylic polymer of non cohesiveness *****, A urethane acrylic water dispersing element to which a modulus of elasticity in tension in a tensile test of the film ghost is characterized by elongation after fracture being not less than 300% 0.5 kg / above mm².

[Claim 2] The urethane acrylic water dispersing element according to claim 1 whose stress survival rate of 1 minute after [when expanding a film ghost 50%] is 40% or less.

[Claim 3] The urethane acrylic water dispersing element according to claim 1 which a polyol ingredient makes polyether polyol or polyester polyol with a subject.

[Claim 4] a) preparing a urethane acrylic hybrid water dispersed matter which consists of a polyol ingredient, a polyisocyanate component, and an acrylic component — b — as acrylic components other than the above to 20 to 90 % of the weight of that solid content to this water dispersed matter, (Meta) Glass transition temperature of polymer which uses acrylic acid alkyl ester as the main ingredients 80 to 10 % of the weight of monomers for adhere[un-]-izing which become 273K or more in addition, by carrying out polymerization, A manufacturing method of a urethane acrylic water dispersing element manufacturing the urethane acrylic water dispersing element according to claim 1 to 3.

[Claim 5] A manufacturing method of the urethane acrylic water dispersing element according to claim 4 which is a monomer from which glass transition temperature of polymer to which a monomer for adhere[un-]-izing uses acrylic acid alkyl ester (meta) as the main ingredients becomes 300K or more in b process.

[Claim 6] In a process, a carboxyl group content urethane prepolymer is compounded using a polyol ingredient and a polyisocyanate component, A monomer which uses acrylic acid alkyl ester as the main ingredients as an acrylic component (meta) at this is mixed, Neutralize a carboxyl group of the above-mentioned prepolymer and water is made to distribute this mixture, A manufacturing method of the urethane acrylic water dispersing element according to claim 4 or 5 which prepares a line intermediary and a urethane acrylic hybrid water dispersed matter for main chain extension of the above-mentioned prepolymer by a reaction of an isocyanate group, and a polymerization of the above-mentioned monomer.

[Claim 7] A polymer which has a carboxyl group and a hydroxyl group in intramolecular to which it comes to carry out copolymerization of the monomeric mixture which used acrylic acid alkyl ester (meta) as the main ingredients, and added a carboxyl group containing monomer to a polyol ingredient as an acrylic component in a process at this is mixed, Make a polyisocyanate component react to this mixture, and an isocyanate prepolymer is compounded, A manufacturing method of the urethane acrylic water dispersing element according to claim 4 or 5 which neutralizes the above-mentioned carboxyl group, makes water distribute this prepolymer, and prepares a line intermediary and a urethane acrylic hybrid water dispersed matter for main chain extension by a reaction of an isocyanate group.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to the urethane acrylic water dispersing element used as a base material of adhesive tape or a medical-application tape, etc., and its manufacturing method.

[0002]

[Description of the Prior Art]By polyol, the kind of polyisocyanate, etc., since physical properties can be changed a lot, polyurethane is used widely industrially. Since acrylic polymer is excellent in weatherability or heat resistance, it is applied widely, but although it is thermoplastic polymer therefore, it is accepted that it is also inferior to temperature sensitive. For this reason, the device which employs the feature of both the above-mentioned polymer efficiently is performed conventionally, and polyurethane using acrylic polyol is examined as a thing excellent in weatherability.

[0003]In JP,H10-53709,A etc., examination of moisture powder type polyurethane is made from the environmental measure side in recent years. However, the problem which the main chain extension in a hyphrogamy body is fully hard to be performed, and it is limited in physical properties, and an organic solvent needs to use necessity, *****, and an emulsifier to make water distribute polyurethane of the amount of Polymer Division, and has an adverse effect on a water resisting property etc. is *****. On the other hand, as for acrylic polymer, the problem which has an adverse effect on physical properties or a water resisting property since it is necessary to use an emulsifier, although an emulsion polymerization is easy and the amount object of Polymer Division can be acquired by that cause is *****.

[0004]As a method of solving such physical properties and a water resisting property, the trial which hybridizes an acrylic and urethane on the US,5,173,526,B Descriptions is made. However, it is hard to be obtained, and the difficulty of acquiring polymer physical properties suitable for the base material of adhesive tape or a medical-application tape, etc. is carried out, and especially the thing that was not easy to adjust the physical properties of polymer also with this method, and was excellent in the extension characteristic is **.

[0005]

[Problem(s) to be Solved by the Invention]In the light of such a situation, this invention by the water dispersing element stably distributed by water without urethane acrylic polymer using an emulsifier *****, It excels in the water resisting property of that film ghost, and it excels in physical properties, such as a mechanical strength and an extension characteristic, and the design of these physical properties aims at providing a urethane acrylic water dispersing element suitable for the base material of easy adhesive tape and medical-application tape, etc., and its manufacturing method.

[0006]

[Means for Solving the Problem]In order that this invention persons may attain the above-mentioned purpose, as a result of inquiring wholeheartedly, a urethane acrylic hybrid water dispersed matter, By that is, a method of adding and carrying out polymerization of the monomer specific as another acrylic component to this, after preparing a water dispersed matter which consists of a complex of a urethane prepolymer and acrylic polymer by a proper technique. If it is made to make urethane acrylic polymer of non cohesiveness generate at a room temperature which has the quantity of a polyol ingredient, a polyisocyanate component, and an acrylic component in a specific range, respectively, A water dispersing element stably distributed by water without the above-mentioned urethane acrylic polymer using an emulsifier is obtained, The film ghost is excellent in a water resisting property, and excellent in physical properties, such as a mechanical strength and an extension characteristic, It knew that a urethane acrylic water dispersing element suitable for a base material of adhesive tape or a medical-application tape, etc. which a design of these physical properties can perform easily by presentation adjustment of the above-mentioned monomer, etc. would be obtained, and this invention was completed.

[0007]This invention by a water dispersing element of urethane acrylic polymer of non cohesiveness at a room temperature which consists of 10 to 50 % of the weight of polyol ingredients, 2 to 20 % of the weight of polyisocyanate components, and 40 to 90 % of the weight of acrylic components Namely, *****, A modulus of

elasticity in tension in a tensile test of the film ghost 0.5 kg / above mm², A urethane acrylic water dispersing element, wherein elongation after fracture is not less than 300% (Claim 1), A urethane acrylic water dispersing element of the above-mentioned composition whose stress survival rate of 1 minute after [when expanding the above-mentioned film ghost 50%] is 40% or less (Claim 2), The above-mentioned polyol ingredient starts a urethane acrylic water dispersing element (Claim 3) of the above-mentioned composition which makes polyether polyol or polyester polyol a subject.

[0008] This invention as a manufacturing method of a urethane acrylic water dispersing element of the above-mentioned composition, a) preparing a urethane acrylic hybrid water dispersed matter which consists of a polyol ingredient, a polyisocyanate component, and an acrylic component — b — as acrylic components other than the above to 20 to 90 % of the weight of that solid content to this water dispersed matter, (meta-) 80 to 10 % of the weight of monomers for adhere[un-]—izing from which glass transition temperature of polymer which uses acrylic acid alkyl ester as the main ingredients becomes 273K or more — in addition, In a manufacturing method (Claim 4) of a urethane acrylic water dispersing element carrying out polymerization, and the above-mentioned b process, Glass transition temperature of polymer to which a monomer for adhere[un-]—izing uses acrylic acid alkyl ester (meta) as the main ingredients is applied to a manufacturing method (Claim 5) of a urethane acrylic water dispersing element of the above-mentioned composition which is a monomer which becomes 300K or more.

[0009] This invention compounds a carboxyl group content urethane prepolymer in the above-mentioned a process using a polyol ingredient and a polyisocyanate component, A monomer which uses acrylic acid alkyl ester as the main ingredients as an acrylic component (meta) at this is mixed, Neutralize a carboxyl group of the above-mentioned prepolymer and water is made to distribute this mixture, A manufacturing method (Claim 6) of a urethane acrylic water dispersing element of the above-mentioned composition which prepares a line intermediary and a urethane acrylic hybrid water dispersed matter is started in main chain extension of the above-mentioned prepolymer by a reaction of an isocyanate group, and a polymerization of the above-mentioned monomer.

[0010] In the above-mentioned a process, to a polyol ingredient, as an acrylic component, (Meta) A polymer which has a carboxyl group and a hydroxyl group in intramolecular to which it comes to carry out copolymerization of the monomeric mixture which used acrylic acid alkyl ester as the main ingredients, and added a carboxyl group containing monomer to this is mixed, Make a polyisocyanate component react to this mixture, and an isocyanate prepolymer is compounded, Neutralize the above-mentioned carboxyl group, water is made to distribute this prepolymer, and a manufacturing method (Claim 7) of a urethane acrylic water dispersing element of the above-mentioned composition which prepares a line intermediary and a urethane acrylic hybrid water dispersed matter is started in main chain extension by a reaction of an isocyanate group.

[0011]

[Embodiment of the Invention] What the polyol ingredient in this invention has two pieces or a hydroxyl group beyond it in one molecule, and made the subject *****, polyether polyol, or polyester polyol is used preferably. As for the molecular weight of this polyol ingredient, it is preferred that the number average molecular weight measured by the gel permeation chromatography (GPC) is in the range of 500–4,000. If the molecular weight of a polyol ingredient is too small, the hard segment of urethane will increase, and when produced polymer becomes hard too much and a molecular weight is too large, it is easy to be inferior to the dispersibility to water.

[0012] The above-mentioned polyether polyol Ethylene glycol, diethylene glycol, Dihydric alcohol, such as propylene glycol, butylene glycol, and hexamethylene glycol, The thing which comes to carry out addition condensation of ethyleneoxide, propylene oxide, the tetrahydrofuran, etc. to low molecule polyols, such as trihydric alcohol, such as trimethylolpropane, glycerin, and pentaerythritol, is used. The above-mentioned polyester polyol Alcohol, such as the above-mentioned dihydric alcohol, dipropylene glycol, 1,4-butanediol, 1,6-hexanediol, and neopentyl glycol, A polycondensation thing with dibasic acid, such as adipic acid, azelaic acid, and sebacic acid, etc. are used.

[0013] As a polyisocyanate component in this invention, each of aromatic series, aliphatic series, or alicyclic polyisocyanates can be used. It is preferred especially to use alicyclic polyisocyanates, such as isophorone diisocyanate, 4,4'-dicyclohexylmethane diisocyanate, the cyclohexane- 1, and 4-JIISOSHINE**TO, from a point of control of a prompt reaction with a polyol ingredient and a reaction with water. Although the above diisocyanate of a polyisocyanate component is preferred, the polyisocyanate more than Tori can also be used for it as occasion demands.

[0014] The acrylic component in this invention uses acrylic acid alkyl ester (meta) as the main ingredients, and what has a carbon number of an alkyl group in the range of 1–14 is preferred as acrylic acid alkyl ester (meta). Specifically Methyl acrylate (meta), ethyl acrylate (meta), (Meta) Acrylic acid propyl, butyl acrylate (meta), acrylic acid (meta) pentyl, (Meta) One sort, such as acrylic acid hexyl, 2-ethylhexyl acrylate (meta), acrylic acid (meta) octyl, acrylic acid (meta) isooctyl, acrylic acid (meta) nonyl, and acrylic acid (meta) isononyl, or two sorts or more are used.

[0015] Other copolymerizable monomers are used among the whole quantity of a monomer with acrylic acid alkyl ester (meta) in the range which does not exceed 50 % of the weight. Specifically Carboxyl group containing monomers, such as acrylic acid (meta), maleic acid, and itaconic acid, Hydroxyethyl (meta) acrylate, hydroxypropyl (meta) acrylate, Hydroxyl group content monomers, such as hydroxybutyl (meta) acrylate, vinyl acetate, Vinyl propionate, styrene or its derivative, acrylamide (meta), Mono-**** of maleic acid Diester, N-methylol(metha)acrylamide, They are glycidyl (meta) acrylate, N,N-dimethylaminoethyl (meta) acrylate, N,N-dimethylaminopropyl(meta) acrylamide, oligoesters (meta) acrylate, epsilon-caprolactone (meta) acrylate, etc. These monomers are also contained in the acrylic component said to this invention.

[0016] In this invention, 10 to 50 % of the weight of the above-mentioned polyol ingredients preferably 20 to 40 % of the weight, 2 to 20 % of the weight of the above-mentioned polyisocyanate components preferably 5 to 15 % of the weight, 40 to 90 % of the weight of the further above-mentioned acrylic components use 50 to 80 % of the weight preferably, It is made to make urethane acrylic polymer of non cohesiveness (in an acupressure grade besides the state which does not show adhesiveness at all, the fine adhesion state which hardly shows adhesiveness is included) constitute from a room temperature, and it is made to distribute this polymer underwater uniformly, without using an emulsifier.

[0017] Here, if a polyol ingredient will be less than 10 % of the weight, ***** and polymer will become hard at the dispersibility to water, and if it exceeds 50 % of the weight, the initial elastic modulus or stress decreasing rate of polymer will not be able to become sufficient easily. Although that amount used is decided corresponding to a polyol ingredient, a polyisocyanate component is inferior to the dispersibility to water, when this amount used will be less than 2 % of the weight, and if it exceeds 20 % of the weight, the elongation of polymer will become small easily. If an acrylic component will be less than 40 % of the weight, the modulus of elasticity in tension and stress decreasing rate of polymer will worsen, and when it exceeds 90 % of the weight, it is easy to be inferior to the dispersibility to water.

[0018] In this invention, the water dispersion of urethane acrylic polymer which is non cohesiveness at the room temperature which consists of the above-mentioned composition, The tensile test of the film ghost produced by applying this and drying (cross-section area: about 2 mm²) Length : The modulus of elasticity in tension by 10 mm, and 300-mm the speed of testing for /More than 0.5 kg / mm². More than 1 kg / mm² are more than 3 kg / mm² (below 30 kg / mm² usually.) more preferably. It is below 20 kg / mm² preferably, and elongation after fracture is preferably characterized by being not less than (usually 3,000% or less, preferably 2,500% or less) 500% more preferably not less than 400% not less than 300%. The stress survival rate of 1 minute after [when the above-mentioned water dispersion expands the above-mentioned film ghost 50%] is preferably characterized also by being 25% or less (usually not less than 15%) more preferably 30% or less 40% or less.

[0019] For this reason, the film ghost obtained from the water dispersion of this invention, As the thing which is excellent in a water resisting property, and is excellent in intensity, an extension characteristic, etc., and a thing which can perform adjustment of these physical properties easily with the presentation of an acrylic component, etc., It can use effectively for the base material of medical-application tapes, such as adhesive tape, a dressing, emergency bonds, and a surgical tape, etc., and, thereby, various effects, such as bolting reduction by reduction of the tape stress at the time of attachment, the occurrence prevention of the float from a terminal, and the stress to adherend, are done so.

[0020] In this invention, at the room temperature which consists of the above-mentioned composition, the water dispersion of urethane acrylic polymer of non cohesiveness, a) preparing the urethane acrylic hybrid water dispersed matter which consists of a polyol ingredient, a polyisocyanate component, and an acrylic component — b — as acrylic components other than the above to 20 to 90 % of the weight of that solid content to this water dispersed matter, (meta-) 80 to 10 % of the weight of monomers for adhere[un]-izing from which the glass transition temperature of the polymer which uses acrylic acid alkyl ester as the main ingredients becomes 273K or more — in addition, it can manufacture easily by carrying out polymerization. Namely, the kind and quantity of each above-mentioned ingredient are chosen only at the above-mentioned a process, Although it is not easy to adjust the dispersibility to the water of urethane acrylic polymer, the non cohesiveness in a room temperature, the intensity of a film ghost and an extension characteristic, a stress survival rate, etc., the above-mentioned characteristic by the above-mentioned selection can be easily adjusted by adding the above-mentioned b process to the above-mentioned a process.

[0021] In a process, the urethane acrylic hybrid water dispersed matter which consists of a polyol ingredient, a polyisocyanate component, and an acrylic component, i.e., the water dispersed matter which consists of a complex of a urethane prepolymer and acrylic polymer, is prepared. A carboxyl group content urethane prepolymer is compounded using ** polyol ingredient and a polyisocyanate component as this method, The monomer which uses acrylic acid alkyl ester as the main ingredients as an acrylic component (meta) at this is mixed, The method of neutralizing the carboxyl group of the above-mentioned prepolymer, making water distribute this mixture, and preparing a line intermediary and a urethane acrylic hybrid water dispersed matter for main chain extension of the above-mentioned prepolymer by the reaction of an isocyanate group and the

polymerization of the above-mentioned monomer is preferred.

[0022]As an option, to ** polyol ingredient as an acrylic component, (Meta) The polymer which has a carboxyl group and a hydroxyl group in the intramolecular to which it comes to carry out copolymerization of the monomeric mixture which used acrylic acid alkyl ester as the main ingredients, and added the carboxyl group containing monomer to this is mixed, Make a polyisocyanate component react to this mixture, and an isocyanate prepolymer is compounded, The method of neutralizing the above-mentioned carboxyl group, making water distribute this prepolymer, and preparing a line intermediary and a urethane acrylic hybrid water dispersed matter for the main chain extension by the reaction of an isocyanate group is also preferred.

[0023]In the method of the above-mentioned **, a carboxyl group content urethane prepolymer is first compounded using a polyol ingredient and a polyisocyanate component. In order to introduce a carboxyl group into a urethane prepolymer as a polyol ingredient here, 2,2-dimethylol propionic acid, 2,2-dimethylol acetic acid, 2,2-dimethylol butanoic acid, etc. other than the aforementioned polyether polyol or polyester polyol are used as carboxyl content polyol.

[0024]It is good to use dibutyl tin dilaurate, OKUTOE acid tin, 1,4-diazabicyclo 2,2,2-octane, etc. as a catalyst in the reaction of such a polyol ingredient and a polyisocyanate component. If the amount of the polyol ingredient used is good to make it a NCO/OH ratio (equivalent ratio) serve as the range of 2-9 to a polyisocyanate component, and, and the stability of a water dispersed matter worsens and becomes excessive, the extension characteristic of the intermediary last polymer with many unreacted polyisocyanate components will worsen. [the amount] [a thing] In order to improve compatibility with an acrylic component, on the occasion of the above-mentioned reaction, hydroxyl group content monomers, such as hydroxyethyl (meta) acrylate, hydroxypropyl (meta) acrylate, and hydroxybutyl (meta) acrylate, may be used together.

[0025]Water is distributed, after mixing an acrylic component to the carboxyl group content urethane prepolymer obtained by carrying out in this way next and neutralizing the carboxyl group of the above-mentioned prepolymer by a base. The monomer which uses the aforementioned acrylic acid alkyl ester (meta) as the main ingredients is used for an acrylic component, the polymer shows adhesiveness to it, ***** also shows non cohesiveness to it, and ***** is also good for it. If the amount of the acrylic component used is good to make it become 20 to 80 % of the weight, and preferably ten to 90% of the weight among the total quantity with a urethane prepolymer, and homogeneous mixing of the monomer for adhere[un-]-izing in b process becomes difficult and becomes excessive, a stable water dispersed matter will be hard to be obtained. [the amount] [a thing]

[0026]As a base for neutralization, it reacts to a carboxyl group, and does not react to an isocyanate group, and, generally tertiary amines, such as sodium hydroxide, a potassium hydrate, and triethylamine, should just be used preferably. The neutralization processing by such a base of a line intermediary is [a line intermediary] also good before mixing after mixing of an acrylic component. What is necessary is to drop the distribution to water, stirring the mixture after neutralizing in the water of the specified quantity which carried out the nitrogen purge, and just to perform it, stirring may use the usual agitator, and a line intermediary is also good using a homomixer, a homogenizer, etc. by necessity.

[0027]Thus, the main chain extension of the above-mentioned urethane prepolymer by the reaction of an isocyanate group after distributing water, The water dispersed matter which made long urethane acrylic core polymer of a line intermediary and chain length generate and by which this core polymer was underwater distributed stably in the polymerization of the above-mentioned monomer which is an acrylic component, i.e., a urethane acrylic hybrid water dispersed matter, is prepared. It is desirable to use polyamine, such as ethylenediamine, propylenediamine, and hexamethylenediamine, and to make it react at a rate used as the equivalent on the occasion of the above-mentioned main chain extension to the isocyanate group which remains. On the occasion of the above-mentioned polymerization, as a radical polymerization initiator, azobisisobutyronitrile, azo compounds, such as azobis isobutyl valeronitrile, and organic peroxide, such as benzoyl peroxide, — per monomer 100 weight section — usually — 0.01 to 5 weight section — desirable — 0.05 — the object for the amount parts of duplexes — what is necessary is *****(ing) and making it just make it react

[0028]In the method of the above-mentioned **, copolymerization of the monomeric mixture which used acrylic acid alkyl ester (meta) as the main ingredients, and added the carboxyl group containing monomer to this as an acrylic component first is carried out, and the polymer which has a carboxyl group and a hydroxyl group in intramolecular is manufactured. As for this polymer, it is good that 3,000-20,000, and a carboxyl group are 0.0007-0.003 Eq [g] /, and the number average molecular weight by GPC is [a hydroxyl group] 0.00005-0.0007 Eq/g. When too high [if a molecular weight is too low, polymer will become hard too much, and], it is easy to be inferior to the dispersibility to water. When there are too few carboxyl groups, are inferior to the dispersibility to water, and it stops distributing, if too large only by absorbing water. When there are too few hydroxyl groups, it is inferior to ***** with the polyol ingredient to a polyisocyanate component, the phase separation of a urethane acrylic component becomes unstable [**** intermediary polymer physical properties], and polymer will become hard if too large.

[0029]Such a polymer can be obtained by using acrylic acid alkyl ester (meta) as the main ingredients, and

carrying out copolymerization of the monomeric mixture which added the carboxyl group containing monomer to this with a conventional method using a polymerization initiator and the chain transfer agent which has a hydroxyl group. (Meta) About acrylic acid alkyl ester and a carboxyl group containing monomer, the aforementioned thing can be used, the copolymer shows adhesiveness, ***** also shows non cohesiveness, and ***** is also good. The molecular weight of a polymer can be easily set as said range by adjusting the amount of the chain transfer agent used which has a hydroxyl group when polymerizing, and choosing polymerization conditions, such as temperature and time. In addition to setting out of this molecular weight, the quantity of the carboxyl group contained in the intramolecular of a polymer can be easily set as said range by adjusting the amount of the carboxyl group containing monomer used.

[0030]The quantity of the hydroxyl group contained in the intramolecular of a polymer can be easily set as said range with setting out of a molecular weight by adjusting the amount of the chain transfer agent used which has a hydroxyl group. If the above-mentioned hydroxyl group will be introduced into the molecular terminal of a polymer when the chain transfer agent which has a hydroxyl group is used, and it introduces into a molecular terminal in this way, The long urethane prepolymer of chain length generates by the reaction of this and a polyisocyanate component, and a good result is obtained by physical properties when Polymer Division quantification is carried out eventually. The hydroxyl group which originates in this monomer as occasion demands with the chain transfer agent which has this hydroxyl group using the above mentioned hydroxyl group content monomer may be made to introduce into the arbitrary positions of polymer intramolecular. Naturally the hydroxyl group introduced into the above-mentioned optional position is also contained in the quantity of the hydroxyl group contained in the intramolecular of the polymer used for this invention.

[0031]As a chain transfer agent which has a hydroxyl group, 2-mercaptoethanol, 1-mercapto-2-propanol, 3-mercapto-1-propanol, p-mercaptophenol, etc. are mentioned. As a polymerization initiator, peroxide system initiators, such as azo initiators, such as 2 and 2-azobisiso BURONI tolyl, benzoyl peroxide, a cumene hydroperoxide, are used. As for these polymerization initiators, optimum dose of the amount used is chosen according to the molecular weight of a polymer, etc.

[0032]It is desirable to perform manufacture of the above-mentioned polymer under existence of a polyol ingredient, that is, to add the chain transfer agent which has an above-mentioned monomeric mixture, polymerization initiator, and hydroxyl group in a polyol ingredient, and to polymerize it. In this method, in order to be able to advance a moderate polymerization reaction stably and for some formed polymers to carry out a graft to a polyol ingredient, without using an organic solvent etc. since a polyol ingredient functions as a polymerization solvent, a result desirable to the compatibility of a polyol ingredient and a polymer is obtained.

[0033]Although a mixture with the polymer which has a carboxyl group and a hydroxyl group by such a method in the intramolecular which comes to carry out copolymerization of the monomeric mixture which used acrylic acid alkyl ester (meta) as the main ingredients, and added the carboxyl group containing monomer to this to a polyol ingredient is obtained, As for the rate of both the above-mentioned ingredients, it is good that a polyol ingredient is [20 to 80 % of the weight and the above-mentioned polymer] 80 to 20 % of the weight, and what is necessary is just to decide suitably the amount of a polyol ingredient and the monomeric mixture used before a polymerization so that it may become such a rate. If, and it is inferior to water dispersibility and becomes excessive, the stability of a water dispersed matter will worsen. [a polyol ingredient] In manufacturing the above-mentioned polymer under the nonexistence of a polyol ingredient, it mixes with a polyol ingredient after a polymerization, and prepares the same mixture as the above.

[0034]Next, a polyisocyanate component is made to react to such a mixture, an isocyanate prepolymer is compounded, the carboxyl group of the above-mentioned polymer is neutralized and water is made to distribute this prepolymer. On the occasion of the above-mentioned reaction, a polyisocyanate component, Since main chain extension serves as **** intermediary hyperviscosity in this stage two to 5 times to the whole quantity of the hydroxyl group in a mixture if too little [a thing / it is good the equivalent and to take preferably for the amount of the equivalent used 2.1 to 3 times and], when moisture powder becomes difficult and becomes excessive, there is a fear of an unreacted polyisocyanate component remaining. What is necessary is for the method which adds and heat-treats proper reaction catalysts, such as dibutyltin dilaurate, just to perform it, after the above-mentioned reaction removes the moisture within the system of reaction. Bases, such as triethylamine and ammonia, are used for neutralization. What is necessary is just to perform distribution by adding water to the above-mentioned prepolymer after neutralization, or adding the above-mentioned prepolymer after neutralization to water, and it is uniformly distributed in that case, stirring.

[0035]After distributing water, main chain extension of the above-mentioned urethane prepolymer by the reaction of an isocyanate group Thus, a line intermediary, Long urethane acrylic core polymer of chain length is made to generate, and this core polymer prepares the water dispersed matter distributed stably underwater, i.e., a urethane acrylic hybrid water dispersed matter. It is desirable to use polyamine, such as ethylenediamine, propylenediamine, and hexamethylenediamine, and to make it react at a rate used as the equivalent on the occasion of the above-mentioned main chain extension here to the isocyanate group which remains in the

above-mentioned urethane prepolymer.

[0036]. In b process, were prepared by the method of ** in the above-mentioned a process, or **. Using the urethane acrylic hybrid water dispersed matter which consists of a polyol ingredient, a polyisocyanate component, and an acrylic component, to this water dispersed matter as acrylic components other than the above, (meta-) the monomer for adhere[un-]-izing from which the glass transition temperature of the polymer which uses acrylic acid alkyl ester as the main ingredients becomes 273K or more — in addition, polymerization is carried out. Here as the above-mentioned urethane acrylic hybrid water dispersed matter, ** By a method, since the carboxyl content polyols (2 and 2-dimethylol propionic acid etc.) of low molecular weight are used, when this remains as unreacted, without reacting to a polyisocyanate component, may have an adverse effect on polymer physical properties, but. ** since the carboxyl group is introduced in the polymer chain of a polymer from the beginning by the method — the above — even if it remains as unreacted, it has the advantage that there are few adverse effects to polymer physical properties, and is especially used for this invention preferably.

[0037]The monomer for adhere[un-]-izing added to such a urethane acrylic hybrid water dispersed matter, (Meta) The glass transition temperature of the polymer used as the main ingredients acrylic acid alkyl ester 273K or more. It is a monomer which becomes 300K or more preferably, and selection use of what shows the above-mentioned glass transition temperature is carried out out of above mentioned acrylic acid alkyl ester (meta) or this, and other copolymerizable monomers. Among the total quantity with the solid content of the above-mentioned hybrid water dispersed matter, 80 to 10% of the weight, such a monomer for adhere[un-]-izing is a rate used as 70 to 20 % of the weight, and is used preferably.

[0038]Namely, as for the above-mentioned monomer for adhere[un-]-izing, 20 to 90 % of the weight of solid content (the aforementioned urethane acrylic core polymer) of a urethane acrylic high Brit water dispersed matter receives to 30 to 80% of the weight preferably, 80 to 10% of the weight, the monomer for adhere[un-]-izing is a rate which will be 70 to 20 % of the weight preferably, and is used. that an aggregate occurs during polymerization when it comes to the outside of a mentioned range **** — etc. — it carries out and a stable water dispersing element is hard to be obtained. The polyol ingredient of the urethane acrylic polymer from which the amount of the above-mentioned monomer for adhere[un-]-izing used is obtained eventually, Each rate of a polyisocyanate component and an acrylic component must be suitably chosen so that said range, i.e., a polyol ingredient, will be 10 to 50 % of the weight, a polyisocyanate component will be 2 to 20 % of the weight and an acrylic component may be 40 to 90 % of the weight. When it comes to the outside of a mentioned range, it is easy to cause trouble in respect of water dispersibility, an elastic modulus, elongation, or stress fall nature etc. as stated above.

[0039]Polymerization adds the monomer for adhere[un-]-izing to a urethane acrylic hybrid water dispersed matter, makes the urethane acrylic core polymer particle of the above-mentioned water dispersed matter fully absorb this monomer, and is performed by the method of adding a polymerization initiator and heat-treating with a conventional method. It is most preferred to use underwater the azo compound which does not generate an ion generation thing as a polymerization initiator, although peroxides and water-soluble azo compounds, such as ammonium persulfate used for a general emulsion polymerization, are used. What is necessary is to mix to the monomer for adhere[un-]-izing beforehand, and just to add, when using an oil-soluble polymerization initiator.

[0040]The urethane acrylic water dispersing element produced by carrying out such, . Distributed uniformly underwater, without urethane acrylic polymer of non cohesiveness using an emulsifier at a room temperature. ***** and its film ghost show the modulus of elasticity in tension excelled and described above to the water resisting property, elongation after fracture, and the above mentioned stress survival rate (stress relaxation nature) by the water dispersing element whose solids concentration is usually 25 to 60 % of the weight. For raising the elastic modulus of a film ghost or coloring etc., if needed, a cross linking agent, a bulking agent, paints, fibrous material, a foaming agent, etc. may be blended with this urethane acrylic water dispersing element, and stabilizer, such as an antiaging agent and an ultraviolet ray absorbent, can also be blended with it.

[0041]Such a urethane acrylic water dispersing element can be applied on a detachability substrate, and thickness can make it the film ghost which is usually 10–200 micrometers by drying. Since this film ghost has the aforementioned characteristic, are independent [this] or as a layered product with other plastic films, paper, etc., Industrial use can be widely used as a base material etc. of medical-application tapes, such as the adhesive tape and dressing of one side or both sides, emergency bonds, a surgical tape, etc. which are stuck on a human body, of course. On the occasion of this use, various effects, such as bolting reduction by reduction of the tape stress at the time of attachment, the occurrence prevention of the float from a terminal, and the stress to adherend, can be revealed. The urethane acrylic water dispersing element of above-mentioned this invention can be used taking advantage of the above-mentioned characteristic also as a coat etc. which are given to various kinds of object surfaces besides a film ghost.

[0042]

[Example]Below, working example of this invention is indicated and it explains more concretely. That it is in below with a part means a weight section. The amount of hydroxyl groups (Eq/g) of a polyol ingredient or a

polymer (acrylic polymer) means the value by which the carboxyl radical weight (Eq/g) of a polymer (acrylic polymer) is measured with the potentiometric titration by an alcoholic potassium hydrate, respectively by NMR. [0043]As working example 1 polyol ingredient, 100 copies (number average molecular weight: 2,500, hydroxyl value:41) of diethylene glycol adipate, The mixture solution of 0.35 copy of hydroxyethyl acrylate was carried out to 12.4 copies of dimethylol propionic acid which dissolved in 31 copies of N-methyl pyrrolidone, the heat deairing was carried out at 80 **, and moisture was removed. Added 49.2 copies of 4,4'-dicyclohexylmethane diisocyanate, and added 0.0298 copy of dibutyl tin dilaurate, it was made to react at 65 ** further for 3 hours, and the carboxyl group content urethane prepolymer was compounded.

[0044]100 copies of butyl acrylates were added and stirred to this urethane prepolymer, and 9.4 copies of triethylamines were further added to this, and it stirred and neutralized. After putting in and carrying out the nitrogen purge of 611 copies of distilled water to another flask for 1.5 hours, the above-mentioned neutralized substance was dropped at this with the dropping funnel. Add 0.02 copy of azobis isobutyl valeronitrile 3 times further [ethylenediamine / four copies of] after this dropping with distilled water, and heat at 60 **, and it is made to react for 2 hours, and is ***** about main chain extension and a polymerization.

[0045]Thus, adding and stirring 467 copies of water further to the obtained urethane acrylic hybrid water dispersed matter. the monomeric mixture for adhere[un-]-izing (glass transition temperature of a copolymer: 319K) which consists of 50 copies of butyl acrylates, and 150 copies of methyl methacrylate — in addition, the urethane acrylic core polymer particle of the above-mentioned water dispersed matter was made to absorb Subsequently, 2 and 2-azobis [2- (2-imidazoline 2-yl)] 0.5 copy of propane was added, under the nitrogen air current, at 60 **, it heated for 3 hours and polymerization was carried out. By this 21 % of the weight of polyol ingredients, 10.5 % of the weight of polyisocyanate components, Urethane acrylic polymer of non cohesiveness obtained the urethane acrylic water dispersing element stably distributed by water at the room temperature which consists of 63 % of the weight (a neutralizer, the main chain extension agent of urethane, etc. are contained in the remaining ingredients) of acrylic components.

[0046]As a monomeric mixture for the formation of working example 2 un-adhering, except having used 20 copies of butyl acrylates, and 180 copies (glass transition temperature of a copolymer: 361K) of methyl methacrylate, Urethane acrylic polymer of non cohesiveness obtained the urethane acrylic water dispersing element stably distributed by water like working example 1 at the room temperature as working example 1 with same quantity of a polyol ingredient, a polyisocyanate component, and an acrylic component.

[0047]To 50 copies of polypropylene glycol (hydroxyl group : 0.00067 Eq/(g)) of the working example 3 number average molecular weight 3,000. The monomeric mixture which consists of 45 copies of butyl acrylates, and five copies of acrylic acid, One copy of 2-mercaptoethanol was added as a chain transfer agent which has a hydroxyl group, 0.05 copy of 2,2-azobisisobutyronitrile was added as a polymerization initiator, the polymerization reaction was performed at 50 ** under the nitrogen air current for 6 hours, and viscous liquid was obtained.

[0048]The peak of the number average molecular weight 3,000 which originates in polypropylene glycol by measurement according [this viscous liquid] to GPC, The peak of the number average molecular weight 7,500 originating in a polymer (acrylic polymer) was accepted, and it was checked that it is a mixture of polypropylene glycol and the above-mentioned polymer. As a result of analysis, the carboxyl group of the above-mentioned polymer is 0.0014 Eq/g, a hydroxyl group is 0.00025 Eq/g, and it is *****.

[0049]Decompression treatment of the viscous liquid which consists of such a mixture is heated and carried out to 100 **, After removing the moisture which remains, added 11.8 copies (it is the 2.3 time equivalent to all the hydroxyl groups) of isophorone diisocyanate, added 0.01 copy of dibutyltin dilaurate, it was made to react at 65 ** for 3 hours, and the isocyanate prepolymer was compounded.

[0050]this isocyanate prepolymer — seven copies (it is an equivalent to a carboxyl group) of triethylamines — in addition — after neutralizing a carboxyl group, while stirring — 150 copies of water — in addition, water was made to distribute the above-mentioned prepolymer subsequently, the solution which diluted 1.8 copies (it is an equivalent to the isocyanate group which remains) of ethylenediamine with 16.2 copies of water — in addition — making it react at 65 ** for 3 hours — main chain extension — *****.

[0051]Thus, adding and stirring 250 copies of water further to the obtained urethane acrylic hybrid water dispersed matter. the monomeric mixture for adhere[un-]-izing (glass transition temperature of a copolymer: 330K) which consists of ten copies of butyl acrylates, and 40 copies of methyl methacrylate — in addition, the urethane acrylic core polymer particle of the above-mentioned water dispersed matter was made to absorb Subsequently, 2 and 2-azobis [2- (2-imidazoline 2-yl)] After having added 0.02 copy of propane, starting the polymerization reaction and holding at 50 ** for 4 hours, temperature up was carried out to 70 **, and it held for 1 hour, and cooled. By such polymerization, 29 % of the weight of polyol ingredients, 7 % of the weight of polyisocyanate components, Urethane acrylic polymer of non cohesiveness obtained the urethane acrylic water dispersing element stably distributed by water at the room temperature which consists of 58 % of the weight (a neutralizer, the main chain extension agent of urethane, etc. are contained in the remaining ingredients) of acrylic components.

[0052]As a monomeric mixture for the formation of working example 4 un-adhering, ten copies of butyl acrylates, Except having used ten copies of ethyl acrylate, and 30 copies (glass transition temperature of a copolymer: 302K) of methyl methacrylate, Urethane acrylic polymer of non cohesiveness obtained the urethane acrylic water dispersing element stably distributed by water like working example 3 at the room temperature as working example 3 with same quantity of a polyol ingredient, a polyisocyanate component, and an acrylic component.

[0053]To 50 copies of polytetramethylene glycols (hydroxyl group : 0.00067 Eq/(g)) of the working example 5 number average molecular weight 3,000. The monomeric mixture which consists of 25 copies of butyl acrylates, 20 copies of ethyl acrylate, 4.5 copies of acrylic acid, and 0.5 copy of acrylic acid 2-hydroxyethyl, One copy of 2-mercaptoethanol was added as a chain transfer agent which has a hydroxyl group, 0.05 copy of 2,2-azobisisobutyronitrile was added as a polymerization initiator, the polymerization reaction was performed at 50 ** under the nitrogen air current for 6 hours, and viscous liquid was obtained.

[0054]The peak of the number average molecular weight 3,000 which originates in polytetramethylene glycol by measurement according [this viscous liquid] to GPC, The peak of the number average molecular weight 7,400 originating in a polymer (acrylic polymer) was accepted, and it was checked that it is a mixture of polytetramethylene glycol and the above-mentioned polymer. As a result of analysis, the carboxyl group of the above-mentioned polymer (acrylic polymer) is 0.0012 Eq/g, a hydroxyl group is 0.00033 Eq/g, and it is *****.

[0055]Decompression treatment of the viscous liquid which consists of such a mixture is heated and carried out to 100 **, After removing the moisture which remains, the isocyanate prepolymer was compounded by adding 15.2 copies (it is the 2.3 time equivalent to all the hydroxyl groups) of 4,4-dicyclohexylmethane diisocyanate, adding 0.01 copy of dibutyltin dilaurate further, and making it react at 65 ** for 3 hours.

[0056]this isocyanate prepolymer — 6.3 copies (it is an equivalent to a carboxyl group) of triethylamines — in addition — after neutralizing a carboxyl group, while stirring — 150 copies of water — in addition, water was made to distribute the above-mentioned prepolymer subsequently, the solution which diluted 1.9 copies (it is an equivalent to the isocyanate group which remains) of ethylenediamine with 17.1 copies of water — in addition — making it react at 65 ** for 3 hours — main chain extension — *****.

[0057]Thus, adding and stirring 280 copies of water further to the obtained urethane acrylic hybrid water dispersed matter. The monomeric mixture for adhere[un-]izing (glass transition temperature of a copolymer: 330K) which consists of 16 copies of butyl acrylates and 64 copies of methyl methacrylate was added, it stirred in the nitrogen air current for 1 hour, and the urethane acrylic core polymer particle of the above-mentioned water dispersed matter was made to absorb. Temperature up is carried out to 50 **, and it is 2 and 2-azobis.

[2- (2-imidazoline 2-yl)] After having added 0.02 copy of propane, starting the polymerization reaction and holding at 50 ** for 4 hours, temperature up was carried out to 70 **, and it held for 1 hour, and cooled. By this polymerization, 24.6 % of the weight of polyol ingredients, 7.5 % of the weight of polyisocyanate components, Urethane acrylic polymer of non cohesiveness obtained the urethane acrylic water dispersing element stably distributed by water at the room temperature which consists of 64 % of the weight (a neutralizer, the main chain extension agent of urethane, etc. are contained in the remaining ingredients) of acrylic components.

[0058]Each urethane acrylic water dispersing element of above-mentioned working example 1-5 was applied on the polyester film which carried out releasing treatment, it dried for 5 minutes at 130 **, and the 50-micrometer-thick uniform film was produced. Using this film, the tensile test was done by the following method, and a modulus of elasticity in tension and elongation after fracture were measured, and the stress survival rate was measured by the following method. These results are as being shown in Table 1, and are *****.

[0059]Sample a <tensile test> film so that it may become cross-section area about 2 mm², and as a tension tester, Using the autograph AGS-50D type (made by Shimadzu), the length of the test sample was 10 mm, the tensile test was done with 300-mm the speed of testing for /, and from the straight-line portion of the beginning of the stress-strain curve at that time, although the following formula was used, the intermediary and the modulus of elasticity in tension were calculated. The intensity (fracture strength) and elongation after fracture at the time of a fracture are read, and it is *****.

$$\text{引張弾性率} = \frac{F/A}{\Delta L/L_0}$$

F: tensile-stress A:cross-section-area deltaL: Variation Lo distorted (elongation) : the initial length of a sample
[0060]<Stress survival rate> As are the same sample as the above-mentioned tensile test, and pull with 300-mm the speed of testing for /, a tensile test is stopped using the same tension tester at the 50% extension time (5 mm), change of subsequent stress is read and it is shown in the following formula, The stress of 1 minute after was made into the stress survival rate to the stress at the 50% extension time.

$$\text{応力残存率} = \frac{\text{1分後の応力}}{\text{50\%伸張時点の応力}} \times 100 (\%)$$

[0061]

表 1

	引張弾性率 (Kg/mm ²)	破断強さ (Kg/mm ²)	破断伸び (%)	1 分後の応力残存率 (%)
実施例 1	5. 1	1. 3 3	4 5 0	2 1
実施例 2	7. 2	2. 3 3	4 0 0	2 9
実施例 3	4. 6	1. 3 5	6 8 0	2 5
実施例 4	3. 8	1. 2 5	8 2 0	2 3
実施例 5	6. 5	1. 8 5	1, 0 0 0	2 3

[0062]So that clearly from the above result by the method of above-mentioned working example 1-5. While urethane acrylic polymer of non cohesiveness being able to manufacture the urethane acrylic water dispersing element stably distributed by water at a room temperature, and according to this water dispersing element excelling in film formability and showing a good water resisting property, without using an emulsifier, It turns out that tractive characteristics (a modulus of elasticity in tension, fracture strength, and elongation after fracture) are what can produce the film which was excellent in stress relaxation nature with a low stress survival rate good.

[0063]

[Effect of the Invention]According to this invention, by the water dispersing element stably distributed by water without urethane acrylic polymer of non cohesiveness using an emulsifier at a room temperature As mentioned above, *****, It excels in the water resisting property of that film ghost, and it excels in physical properties, such as a mechanical strength and an extension characteristic, and a urethane acrylic water dispersing element suitable for the base material of adhesive tape and a medical-application tape with an easy design of these physical properties, etc. and its manufacturing method can be provided.

[Translation done.]